Subdocument Technical Procedure

Analysis of Methane in Air

version 1.2

filename: TP_analysis_CH4_v1.2.1.pdf

Approved by

1 Oct 2015

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Analysis of Methane in Air

GMD Technical Procedure

Contents

1. Purpose

This document provides the technical procedures for the analysis of methane (CH_4) in air by gas chromatography with flame ionization detection. Methane amount of substance is expressed as dry air mole fraction, and is traceable to the SI unit amount of substance fraction.

2. Scope

NOAA ESRL GMD provides compressed gas standards to the WMO GAW community. Natural air or modified natural air standards are analyzed for CH_4. Methane dry air mole fractions are determined by gas chromatography with flame ionization detection, relative to the WMO CH_4 X2004A scale, maintained by NOAA. The CH_4 calibration scale is derived from gravimetrically-prepared primary standards (see TP_primary_gravimetry_v1.2.pdf). The procedures described here only pertain to CH_4 analysis for which a certificate of analysis is issued.

3. References

Dlugokencky E.J., R.C. Myers, P.M. Lang, K.A. Masaire, A. M. Crotwell, K.W. Thoning, B.D. Hall, J.W. Elkins, and L.P. Steele (2005), Conversion of NOAA atmospheric dry air CH_4 mole fractions to a gravimetrically prepared standard scale, *J. Geophys. Res.,* 110, D18306, doi: 10.1029/2005JD006035.

Dlugokencky, E.J., L.P. Steele, P.M. Lang, and K.A. Masarie (1994), The growth rate and distribution of atmospheric methane, *J. Geophys. Res,.*99, 17,021-17,043.

JCGM (2008), International vocabulary of metrology – Basic and general concepts and associated terms (VIM), JCGM 200:2008.

JCGM 100:2008 Evaluation of Measurement Data – Guide to the Expression of Uncertainty in Measurement (ISO GUM 1995 with minor corrections), Joint Committee for Guides in Metrology (2008); http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf

Salameh, P.K., Scripps Institution of Oceanography, Unix-based Integrator and Chromatographic Database, personal communication, 1997.

4. Terms and Definitions

analysis system: Includes the gas chromatograph, hardware, software, and computer used to analyze CH_4 in compressed gas cylinders (synonymous with measuring system**)**.

gas standard: A cylinder of compressed gas with mole fractions assigned by metrological methods or by comparison to higher-level standards, used to characterize the response of an instrument for calibration or quality control purposes. For the purposes of this TP, primary, secondary, and tertiary standards are gas standards.

mole fraction: The ratio of the number of moles of analyte to the total number of moles. Dry air mole fraction is the ratio of the number of moles of analyte to the total number of moles in dry air. Within the scope of this TP, all samples are analyzed for dry air mole fraction.

primary standard: A measurement standard established using a primary reference measurement procedure, or created as an artifact, chosen by convention.

reference: Dry, natural air in a high-pressure cylinder with near-ambient CH_4 mole fraction used to normalize variations in temperature and pressure through an analysis period.

regulator: A device used to reduce the pressure in a gas cylinder (input) to a lower pressure (output). High-purity and ultra-high purity regulators are used.

secondary standard: A standard whose value is determined through analysis relative to primary standards, for a quantity of the same kind. These standards are used to calibrate the instrument response. Use of secondary standards for routine calibration prolongs the life of primary standards. For CH_4, values for secondary standards may also be assigned by comparison to other secondary standards, with verification performed by comparison to primaries.

target tank: A target tank is used for routine monitoring of system performance. The system should be capable of reproducing the assigned value of the target tank (within expected uncertainties).

tertiary standard: Measurement standard established through calibration with respect to secondary measurement standards for a quantity of the same kind.

WMO/GAW: World Meteorological Organization, Global Atmosphere Watch.

working standard: Gas standard used to calibrate the analysis system, typically a secondary standard.

5. Procedures

5.1 Gas Handling

Cylinders to be analyzed are stored in a common location and moved to the CH_4 analysis room when needed. Prior to analysis, a regulator is attached. Several regulators models are used. For CH_4, regulator purity is generally not an issue although high purity or ultra-high purity low flow regulators are preferred to preserve the integrity of other trace gases that might be compromised with sub-standard regulators. Upon connecting the regulator, the residual gas in the regulator is purged (flushed) with air from the cylinder. It is left to the analyst to determine the amount of flushing required, as it depends on the history of the regulator and the mole fraction of the gas being analyzed. The cylinder to be analyzed is connected to one of the analysis ports on the analysis system. The output pressure of the regulator should be set to ensure adequate flow rates for sample loop flushing (determined by the analyst).

5.2 Analysis System

The methane analysis system is described in Dlugokencky et al. (1994, 2005). Briefly, gas samples are loaded into a fixed-volume stainless steel loop, and injected onto a packed column. Methane is separated from other compounds and detected by flame ionization detector. The response of the detector is calibrated off-line, as needed, with a suite of secondary standards by measuring the response of each secondary standard relative to reference air. Aliquots of air from each secondary standard are bracketed by aliquots of reference in an A-B-A-B-A ... manner (A = secondary standard and B = reference). The reference is dry natural air at Northern Hemisphere continental background CH_4 mole fraction. The response function of the detector is defined as a fit of the assigned value for each secondary standard vs. the mean normalized peak response. Uncertainties in y-axis parameters are the uncertainties (68% c.i.) in the assigned values of the secondary standards, and uncertainties in x-axis parameters are standard deviations of the normalized response ratios. For calibration of cylinders of air with unknown CH_4 mole fraction, the unknown is also bracketed by aliquots of reference air (A = reference air and B= unknown). A computer program controls the stream selection valve and gas sample valve, and it stores the data from the detector (through the electrometer and analog to digital converter). Operating conditions should not be changed without just cause. CH_4 results are sensitive to flow rates and quality of the carrier and flame gases. The performance of the system should be verified following major changes.

To determine the mole fraction of CH_4 in a cylinder, the cylinder should be run against the working standard on at least two occasions. The number of injections of each run is determined by the analyst. The analyst should compare the results from two independent runs.

The amount of CH_4 is determined by comparing the response (peak area or height) of the unknown sample to that of the working standard. Peak height and peak area are determined using custom integration software (Salameh, 1997).

5.3 Quality Control

It is critical that assignments made using the analytical system are reproducible. For a sample mole fraction that does not change with time, the system must be capable of reproducing the assigned value (within uncertainties) over the long term.

The experienced analyst can easily determine when the system is performing normally. Indicators of performance include, but are not limited to, day-to-day variability of the baseline, repeatability of 6-10 repeat injections of a known or unknown mole fraction, peak shape, and baseline noise. Long term target tanks are measured each year, and short-term targets are measured more frequently. Target tanks are a key indicator of system performance, as long as drift in the assigned CH_4 mole fraction can be determined or ruled out. Additionally, cylinders with known CH_4 (previously analyzed on the system) can also be used to assess performance.

6.0 Calculations

6.1 Mole Fraction

Ratios of unknown and reference peak areas are used to calculate mole fractions from a response function. We typically ratio each aliquot of the unknown peak response (S) to the average peak response of the bracketing reference (R) aliquots.

$$CH_4 = c_0 + c_1 \chi^{c2} \qquad (1)$$

(where c_i are the coefficients of the fit to the secondary standards and x is the response ratio as described by equation 2; when $c_2 = 1$, the function reduces to a linear polynomial).

$$\chi = S/((R1+R2)/2) \qquad (2)$$

We get the same result, within measurement uncertainties, using peak height and peak area. Peak area is the preferred variable to use, however peak height may be used on analyst discretion when conditions warrant.

The NOAA CH_4 calibration scale is derived from a suite of gravimetrically-prepared primary standards. The scale was transferred to a set of secondary standards in 2013 - 2015 using the methods described above but with response curves based on the primary standards.

6.2 Uncertainties

Two estimates of uncertainty are reported for each sample. The first is the expanded uncertainty associated with the value assignment (see TP_primary_gravimetry.docx), and is derived from uncertainties in the primary standards that define the scale, scale transfer, and any other significant uncertainties. Expanded uncertainties are calculated using the GUM (JCGM, 2008) as a guide. The second quantity reported is the long-term reproducibility of the system based on repeated analysis of multiple cylinders (95%ile). Reproducibility is an estimate of our ability to propagate the scale over time periods of several years. It provides an estimate of our ability to detect possible drift in cylinders over time scales of typical use, and is useful for assessing the role of reference materials with respect to inter-laboratory compatibility. The long-term reproducibility of the system based on repeated analysis of tertiary standards is approximately 1 ppb (95%ile) (see Appendix).

7.0 Data Collection and Storage

Processed data and metadata are stored on a centrally located computer in a relational database. The raw data (chromatograms) are archived in text files on a networked server. The database is backed up once a day. The raw data server has a full back up every 2 weeks and incremental back ups every work day. The results (processed data) are also available from a web interface and can be accessed by users according to the cylinder serial number.

8.0 Safety

It is NOAA policy to follow safe working practices when handling compressed gas cylinders and laboratory chemicals. Pressurized cylinders should be secured (except when they are being weighed). Personal protective equipment (PPE) should be used when working with hazardous chemicals or in a high noise environment.

9.0 Documentation

Notes pertaining to cylinder analysis are recorded in a notebook dedicated to the analysis system. For each analysis, the cylinder number and date of analysis should be recorded, along with any variables likely to affect the result. It is left to the analyst to determine which, if any, additional data should be recorded.

10.0 Appendix

10.1 Sample Calculations (mean mole fraction)

Sample calculations are shown in Table A1 for a typical analysis, using area ratio to calculate mole fraction (X_i). Port R is the working standard and port S is the unknown. The unknown was analyzed 20 times in one day. Area and height ratios are determined from the response of the

unknown and the average response of the reference aliquots immediately before and after the unknown.

Table A1:Data used to compute mean CH_4 dry air mole fraction in a gas cylinder with unknown CH_4 mole fraction.(See equation 1 in section 6.1)

Date	Time	Port	BC	Area	Area Ratio (χ)	[CH4] sample
2015 07 23	10 02	R	BB	8.223938E+06		
2015 07 23	10 06	S	BB	8.214265E+06	0.998743829	1852.01
2015 07 23	10 09	R	BB	8.225255E+06		
2015 07 23	10 12	S	BB	8.211351E+06	0.998479849	1851.52
2015 07 23	10 15	R	BB	8.222450E+06		
2015 07 23	10 18	S	BB	8.212899E+06	0.998796698	1852.11
2015 07 23	10 21	R	BB	8.223137E+06		
2015 07 23	10 24	S	BB	8.213811E+06	0.998810313	1852.13
2015 07 23	10 27	R	BB	8.224052E+06		
2015 07 23	10 30	S	BB	8.218571E+06	0.999377895	1853.19
2015 07 23	10 33	R	BB	8.223322E+06		
2015 07 23	10 36	S	BB	8.218951E+06	0.999258728	1852.97
2015 07 23	10 39	R	BB	8.226774E+06		
2015 07 23	10 42	S	BB	8.212959E+06	0.998277043	1851.14
2015 07 23	10 45	R	BB	8.227494E+06		
2015 07 23	10 48	S	BB	8.209452E+06	0.998316733	1851.21
2015 07 23	10 51	R	BB	8.219094E+06		
2015 07 23	10 55	S	BB	8.212066E+06	0.998681792	1851.89
2015 07 23	10 58	R	BB	8.226717E+06		
2015 07 23	11 01	S	BB	8.209046E+06	0.998176626	1850.95
2015 07 23	11 04	R	BB	8.221366E+06		
2015 07 23	11 07	S	BB	8.205556E+06	0.998035991	1850.69
2015 07 23	11 10	R	BB	8.222041E+06		
2015 07 23	11 13	S	BB	8.213534E+06	0.998867667	1852.24
2015 07 23	11 16	R	BB	8.223649E+06		
2015 07 23	11 19	S	BB	8.209367E+06	0.998169658	1850.94
2015 07 23	11 22	R	BB	8.225192E+06		
2015 07 23	11 25	S	BB	8.208682E+06	0.998303159	1851.19
2015 07 23	11 28	R	BB	8.220077E+06		
2015 07 23	11 31	S	BB	8.205683E+06	0.998704835	1851.94
2015 07 23	11 34	R	BB	8.212572E+06		
2015 07 23	11 37	S	BB	8.207163E+06	0.999034217	1852.55
2015 07 23	11 41	R	BB	8.217622E+06		
2015 07 23	11 44	S	BB	8.209260E+06	0.998427912	1851.42
2015 07 23	11 47	R	BB	8.226750E+06		
2015 07 23	11 50	S	BB	8.207671E+06	0.998271806	1851.13
2015 07 23	11 53	R	BB	8.217010E+06		
2015 07 23	11 56	S	BB	8.205683E+06	0.998522602	1851.60
2015 07 23	11 59	R	BB	8.218638E+06		
2015 07 23	12 02	S	BB	8.211840E+06	0.999280947	1853.01
2015 07 23	12 05	R	BB	8.216860E+06		
Summary	N=20		Mean		0.99862691	1851.79
Standard Deviation				0.0004	0.74	

10.2 Reproducibility

Reproducibility is estimated from the 95th percentile of differences from repeated analysis of tertiary standards. From 798 pairs of analyses performed from 1994-2013 (Figures A1, A2) we estimate the reproducibility to be 1 ppb (95%ile).

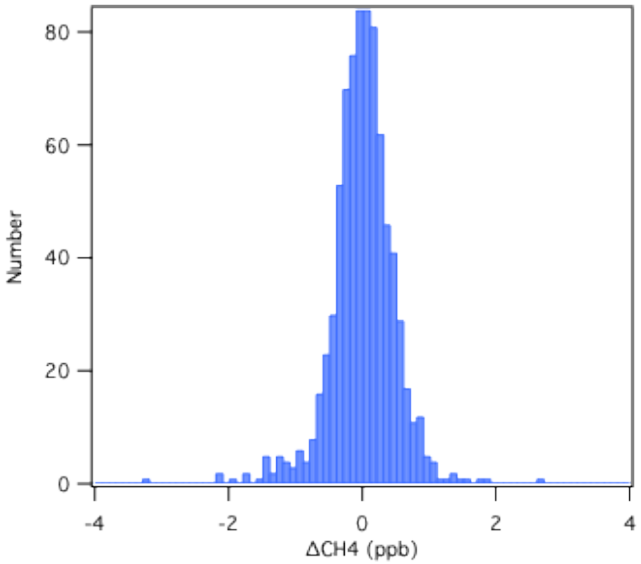

Figure A1: Histogram of differences between initial and subsequent CH_4 measurements of tertiary standards occurring more than one year apart. Data were restricted to analyses between 1994 and 2013 and CH_4 differences less than 5 ppb (to exclude obvious analytical or sampling problems). The 5 ppb restriction results in the exclusion of one outlier.

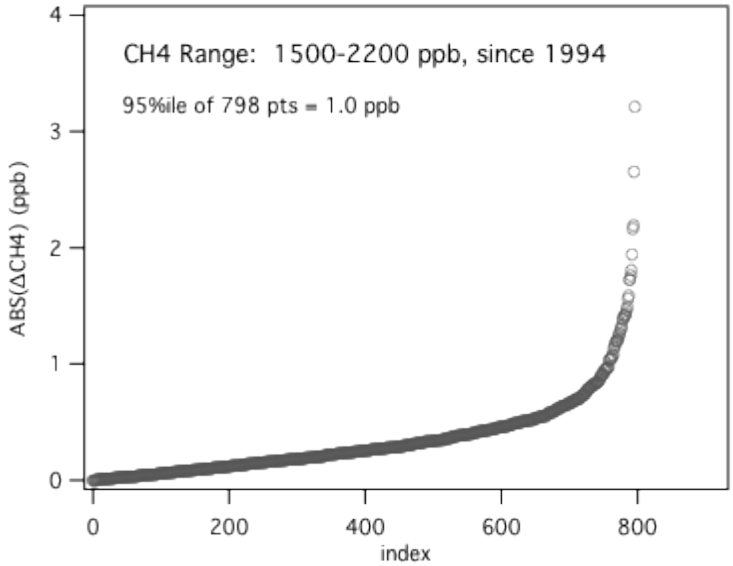

Figure A2: Absolute differences between initial and subsequent analyses occurring more than one year apart, subject to the same restrictions as in Figure A1.

10.3 List of Equipment

Item	Manufacturer	Model Number
Gas Chromatograph	Agilent Technologies	6890
Controller	Agilent Technologies	V34970A
Computer		
Analog/Digital Interface	Agilent Technologies	35900E
Valves and Actuators	Valco	E60, various